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13. ABSTRACT (Maximum 200 words) Electrochemical and spectroscopic studies of tungsten were conducted in a molten fluoride bath. Oxides were removed by treating the melt with HF gas. The residual oxide content was quantitatively determined using $KBrF_4$ and a zirconia cell apparatus. The reaction products of WF_6 and FLINAK were examined using Raman spectroscopy. DTIC QUALITY INSPECTED 2				
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Electroplating of Refractory Metals Using Haloaluminate Melts.

August 15, 1996

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The main objective of this research, performed by Sven E. Eklund, a graduate student at the University of Tennessee, Knoxville, is to explore the fundamentals of electroplating of refractory metals, such as tungsten and tantalum, from the LiF-NaF-KF eutectic and to compare with electroplating of these elements from chlorofluoroaluminate melts.

A considerable amount of interest has been generated in the electrochemistry and metallurgy of the refractory metals of Groups IV-B, V-B, and VI-B due to their potential use in electronic components, electrical devices, and the aerospace industry. Dense, fine grain, structurally coherent plates were originally obtained by a method developed by Mellors and Senderoff [1] in 1964. This method uses electrolytic reduction to the metal from the ternary eutectic LiF-NaF-KF, or FLINAK. Metal deposits obtained by this method have a density of at least 98 per cent of the theoretical density and are substantially free of non-metallic impurities [2,3]. Mechanisms proposed in several articles by Senderoff and coworkers for the reduction of these metals [4-7] have spurred research into the refractory metals in molten fluorides.

Most of our studies of refractory metals have been performed in alkali chloroaluminates. By comparison with FLINAK, sodium chloroaluminate ($\text{AlCl}_3\text{-NaCl}$) melts may be considered as favorable systems in several respects. First, the liquidus temperatures for chloroaluminates lie below 200°C for melt compositions in the range from 49.8 to 100 mole percent AlCl_3 , while FLINAK has a eutectic point of 454°C , and generally temperatures in excess of 750°C are required for refractory metal deposition. The Lewis melt acidity can be varied over a broad range by changing the AlCl_3 to NaCl ratio. Finally, the highly aggressive nature of fluoride melts and the temperatures required for their use greatly limit the materials which can be used for bath construction, whereas chloroaluminate studies can be conducted using even simple Pyrex cells. However, tungsten and tantalum form many cluster species with chloride, making it necessary to use fluoride containing melts only, hence the use of FLINAK in these studies.

Studies of the reduction of tantalum (V) [8], niobium (V) [9], and tungsten (VI) [10], in acidic (AlCl_3 -rich) alkali chloroaluminates show that low oxidation state cluster species, such as $\text{Ta}_6\text{Cl}_{14}$ and W_6Cl_{12} , are formed which, due to high stability and/or insolubility in the melt, prevent further reduction to the metal. In basic (usually $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$) melts, problems can arise because of small amounts of oxide-containing species. This contamination by oxides, arising either from atmospheric impurities or attack of Pyrex by the melt, can be greatly reduced by passing phosgene or carbon tetrachloride through the melt [11,12].

Two methods of purifying FLINAK, to remove oxides in the form of carbonates and sulfates, were attempted. In the first method, the individual FLINAK components were recrystallized by slow cooling at a ramp rate of 4° C/hour. The pure outer crystals were removed and used to make FLINAK while the contaminated inner crystals were discarded. The second method used a purge of hydrogen fluoride gas through the molten FLINAK. Both methods were tested with the tantalum probe technique [13] which uses Raman spectroscopy on the solid samples. With this technique the tantalum oxide and tantalum fluoride band intensity ratio is measured to give an estimate of the oxide content. The results suggested the HF purification yielded more pure FLINAK, but the tantalum probe technique is not exact, so an alternate oxide detection apparatus needed to be developed.

A new method for quantitatively determining oxide was designed which combines the reaction of potassium bromotetrafluoride [14] with a fluoride salt sample to release the oxide in the salt as oxygen gas into the reaction vessel with the use of a closed, Monel tubing loop containing a circulating fan and a platinum-coated zirconia tube. The fan circulates the oxygen through the zirconia tube which is maintained at 800°C. A potential of less than 1 volt is applied across the zirconia tube which then selectively and quantitatively "pumps" out the oxygen from the loop. The amount of oxygen is calculated from the number of coulombs generated.

Studies of tungsten hexafluoride combined with FLINAK have shown that the WF_6 adds around 18 mol% between 650° - 700°C. The major product is K_2WF_8 when the tungsten is unreduced. The role of oxide in the formation of mixed oxidation states of tungsten will be further investigated by additions of Na_2O followed by analysis of the products. Tungsten metal will be used to reduce the WF_6 to a lower oxidation state as it dissolves in the molten FLINAK.

A nickel cell for the electrochemical experiments has been constructed which uses reducing unions with Teflon inserts to insulate the electrodes and allow vacuum and pressure connections. Various base metals such as steel and nickel will be used as electroplating substrates. Platinum will be used as a quasi-reference electrode. Boron nitride has been previously used as a stable reference electrode but has been recently shown to react with some of the refractory metal species in FLINAK [15].

This project will continue by further investigating the quantitative determination of residual oxide in the fluoride salt, and electrochemical and spectroscopic characterization of the tungsten electroplating process.

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Publications

No publications have, as yet, come from this work. This work will continue, however, after the termination of this contract. If any publications are accepted, based on the work supported by your agency, we will send this information to you.